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26 March 2002

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SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2002-070**
Capt. Rene Gonzalez; Brent Viers, et al. (PRSM), "Monofunctional Aminophenyl Polyhedral
Oligomeric Silsesquioxanes (POSS) - A Model for High Performance Nanocomposite Monomers"

(Statement A)

Materials Research Society Meeting
(1-5 April 2002)

Monofunctional Aminophenyl polyhedral oligomeric silsesquioxanes -A model for high performance nanocomposite monomers.

Gonzalez, Rene. I; Viers, Brent D.; Haddad, Timothy
Polymer Working Group-Propulsion Materials
Air Force Research Laboratory AFRL/PRSM
Edwards AFB CA 93524

Abstract:

An aminophenyl functionalized polyhedral silsesquioxane (POSS) was synthesized as a model monofunctional organic-inorganic hybrid monomer. A multistep procedure whereby an incompletely condensed POSS triol scaffold was "corner capped" with phenyltrichlorosilane, and then the phenyl moiety was nitrated and subsequently reduced with Zn/HCl to form the desired aminophenylPOSS (POSS aniline). Mononitration and quantitative reduction to a monoamine was observed. Furthermore, the amine was isolated as the free base, and not as a salt. However, ^1H COSY NMR spectroscopy indicates that a variety of POSS aniline isomers are formed, ortho disubstitution most prevalent (57%), with meta (38%), and para (5%).

Introduction:

Polyhedral oligomeric silsesquioxanes (POSS) are a unique class of nanostructured chemicals that consist of an inorganic silsesquioxane core with an organic R group corona. These materials have most often been used to form organic-inorganic "nanocomposites" with polymeric matrices having improved properties such as increased heat distortion temperatures, enhanced flame and ablation retardance, improved mechanical properties, etc.[1] The traditional method for forming reactive POSS monomers has been to take an incompletely condensed POSS "core" and subsequently react with a suitably functionalized moiety. Feher and coworkers have formed a high performance diaminophenyl POSS monomer (POSS dianiline) via an elegant multistep synthesis.[2] The synthetic reactions involved are moisture and air sensitive, must be carried out under inert atmosphere and include an amine protecting step. High performance space survivable Kapton type polyimides have been formed by condensing the Feher POSS dianiline with pyromellitic dianhydride (PMDA) and oxydianiline (ODA) to form a transparent nanocomposite with enhanced atomic oxygen resistance. [3]

Recently, Laine and coworkers have popularized "nanobricks" formed by functionalizing a completely condensed octaphenyl POSS into an octa(aminophenyl) POSS via nitration of the phenyl groups, and subsequent reduction of the nitro groups to the amine. The octa(aminophenyl) silsesquioxane was shown to form epoxies with enhanced modulus above the glass transition[4]. Polyimides based on the Laine "nanobrick" have also been reported.[5]. The Laine synthesis is more amenable to large scale synthesis, however, this process has only been applied to forming plurifunctional species, and it is unknown whether the synthesis can be controlled to form well defined isomers.

In this communication, monofunctional aminophenyl POSS molecules are prepared. A single phenyl group is introduced to the POSS cage via the traditional method of "corner capping" an incompletely condensed POSS triol with phenyltrichlorosilane. The R group corona of the POSS triol was chosen to be cyclopentyl due to the ease of isolation of the POSS compounds. The phenyl group was converted to an aminophenyl species via nitration and reduction of the nitro group

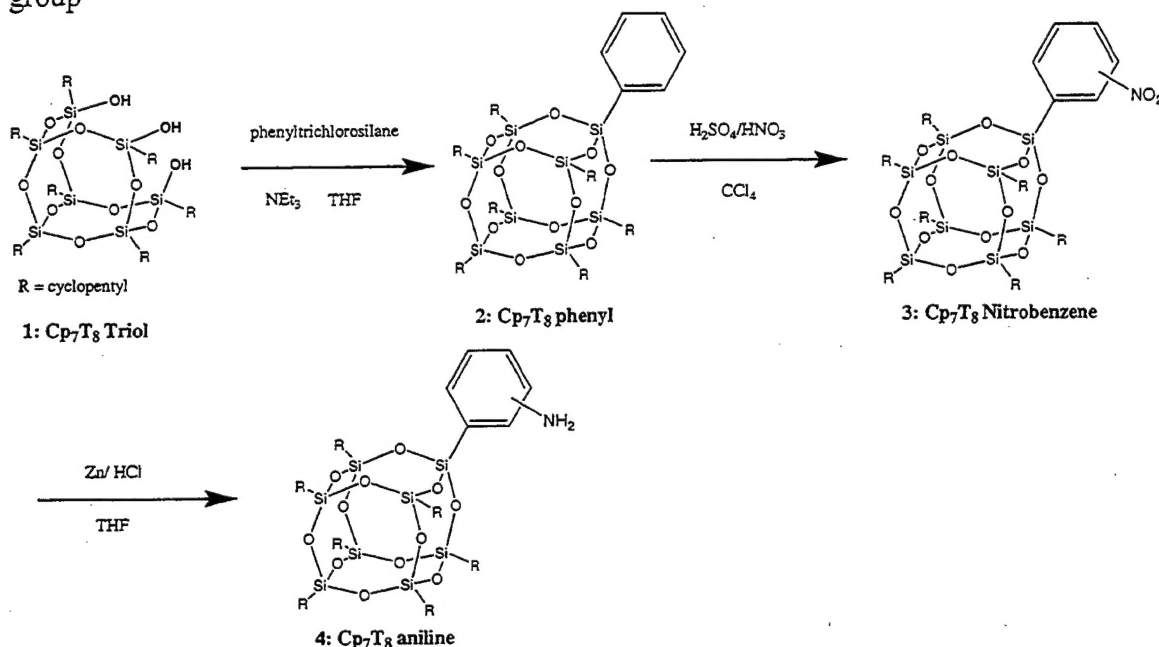


Figure 1). This model compound allowed for an unambiguous characterization of the isomers formed (in particular the complicated phenyl proton resonances in the ¹H NMR spectrum.) This monofunctional species might have use as an endcapping group in polyimide synthesis, but it is anticipated that similar synthetic protocols and characterization would apply to formation of multifunctional POSS materials.

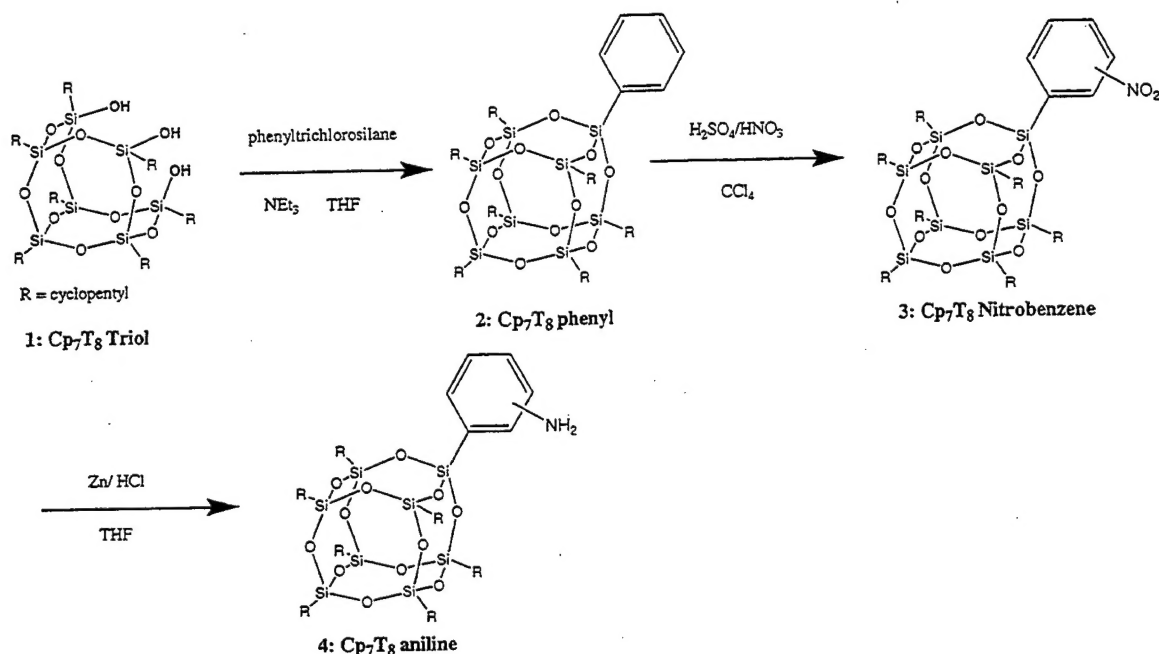


Figure 1 Synthetic Scheme for formation of monofunctional POSS aniline

Experimental:

The corner capping synthesis of cyclopentyl triol POSS to phenyl POSS, nitration and amination of the phenyl species are nominally similar to established techniques [1,4] and will not be elaborated upon here, but in a separate publication. Instead, the spectroscopic characterization of the isomers of the intermediate nitro and final amine compounds will be the focus of this study.

The cyclopentyl POSS-triol silanol, 1 was obtained from Hybrid Plastics Inc. (<http://www.hybridplastics.com>) All NMR spectra were collected on either a Bruker 300 or 400 MHz instrument and obtained from CDCl_3 solutions. ^1H , ^{13}C and ^{29}Si NMR spectra (reported in ppm using the δ scale) were referenced to residual CHCl_3 at 7.26 ppm, to CDCl_3 at 77.0 ppm, and to external SiMe_4 at 0 ppm, respectively. For simplicity, the POSS structures will be abbreviated in the common manner using the silsesquioxane T ($\text{SiO}_{3/2}$) formalism and common chemical functional group names (See Figure 1). The phenyl proton positions are referenced relative to the POSS group, whereas the disubstitution isomers refer to the relative placement of the nitro(amine) relative to the POSS cage.

HPLC were obtained on a HP 1090 Liquid Chromatograph by injecting 10 μL of a 5 ppt sample onto a polyvinylalcohol-silicagel column and eluting at 1 mL / minute using a 5 vol % THF / 95 vol % cyclohexane mobile phase and a Varex MKIII evaporative light scattering detector.

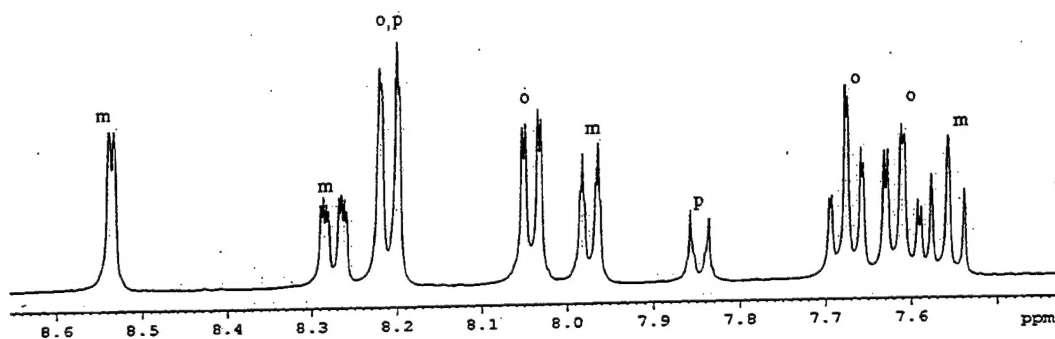
Results and Discussion:

The ^1H NMR spectrum of the nitrobenzene POSS (3) species had a multiple benzene resonances with complicated splitting patterns (FIGURE). This strongly suggests multiple structural isomers. Two dimensional ^1H - ^1H COSY NMR experiments of the nitration product 3, Cp_7T_8 nitrobenzene, and the reduction product 4, Cp_7T_8 aniline, revealed that these monomers are a mixture of the meta, para and ortho isomers. Figure 2 shows the aromatic region of the ^1H NMR spectra of 3 with the peaks assigned to the corresponding isomers. Figure 2 shows the two dimensional ^1H - ^1H COSY NMR of this region. This experiment, along with proton homonuclear decoupling experiments provided sufficient information to adequately assign peaks corresponding to the meta, ortho or para isomer of Cp_7T_7 nitrobenzene 3. Analysis of this data and calculations based on the integral values of the ^1H NMR of the aromatic region reveal that 3, is a mixture of the para (8%), meta (37%) and ortho (55%). This agrees well with calculations based on ^{13}C NMR which result in the ratio of ortho, meta and para to be 50%, 43% and 7% respectively, and the results of HPLC (Figure 3). These results are interesting because the POSS cage has been shown to be electron withdrawing, and electron-withdrawing groups are considered to be meta directors (REF). However, in this case a significant amount of the ortho isomer is present. Even more surprising is the fact that if in this case the POSS cage is also directing ortho and para, that the sterically-hindered ortho would be the more predominant isomer. The aggregate NMR integration also suggests that mononitration deactivates the cage toward further substitution.

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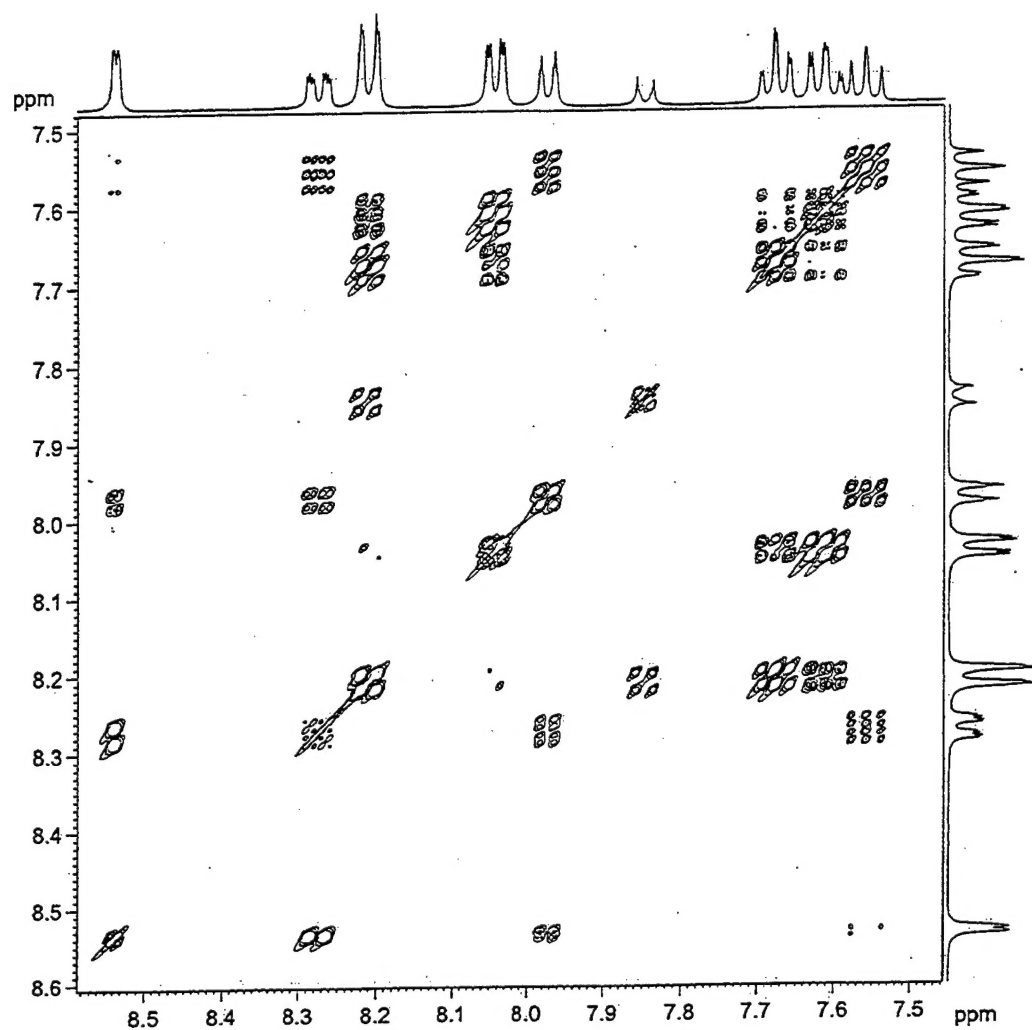


Figure 2 a. Proton NMR of nitrobenzene POSS monomer (top) COSY spectrum (bottom)

↓
Fig. 2a not
mentioned

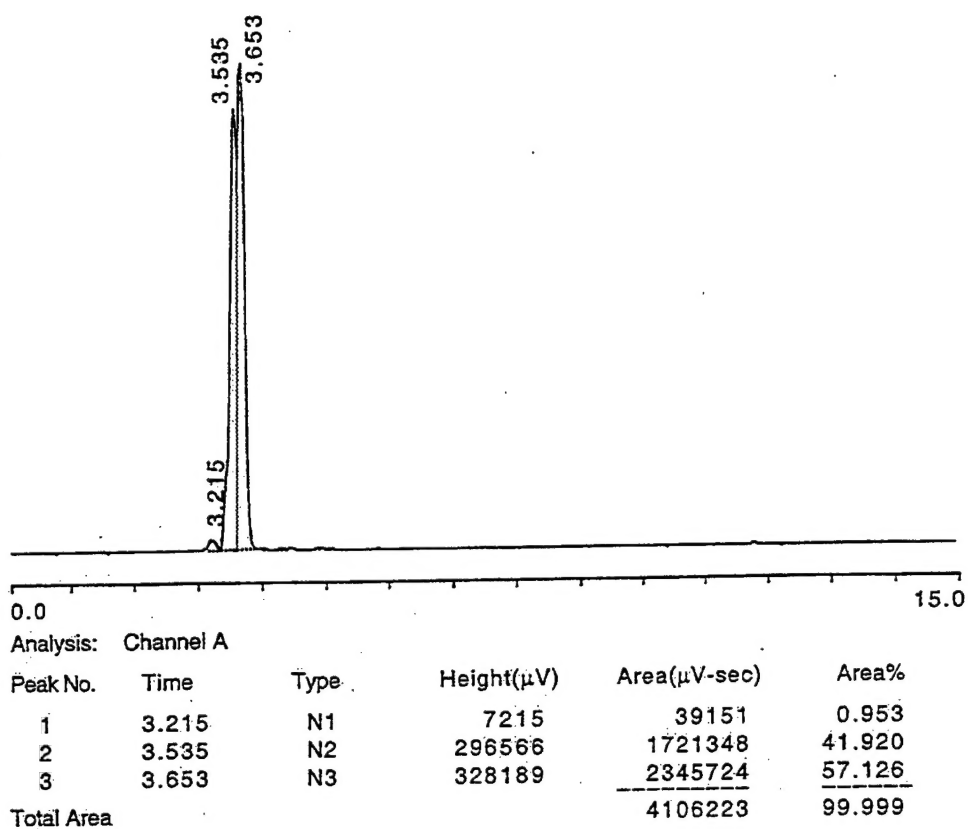
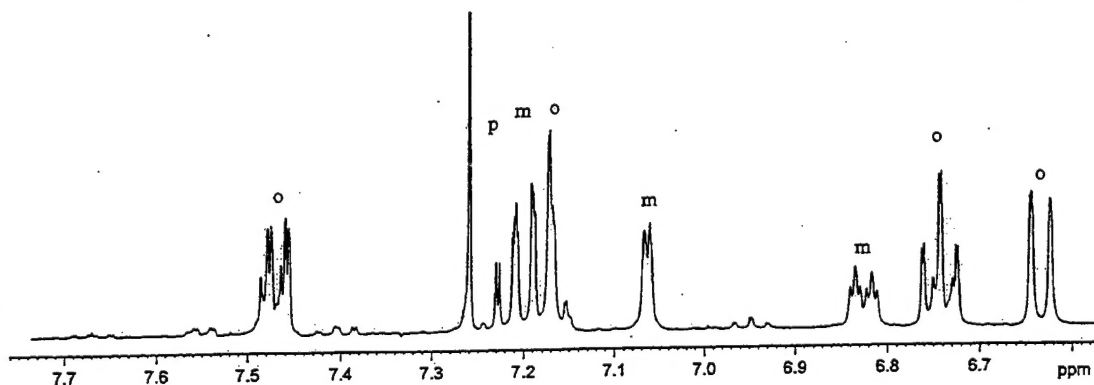


Figure 3 HPLC of nitrobenzene POSS 3

Figure 4 shows the aromatic region of the ^1H NMR spectra of 4 with the peaks assigned to the corresponding isomers. As expected, the spectrum is best described as a mixture of ortho(57%), para (5%), and meta(5%) isomers, which is consistent with the population of the precursor nitrobenzene POSS 3.



67% ?
↑

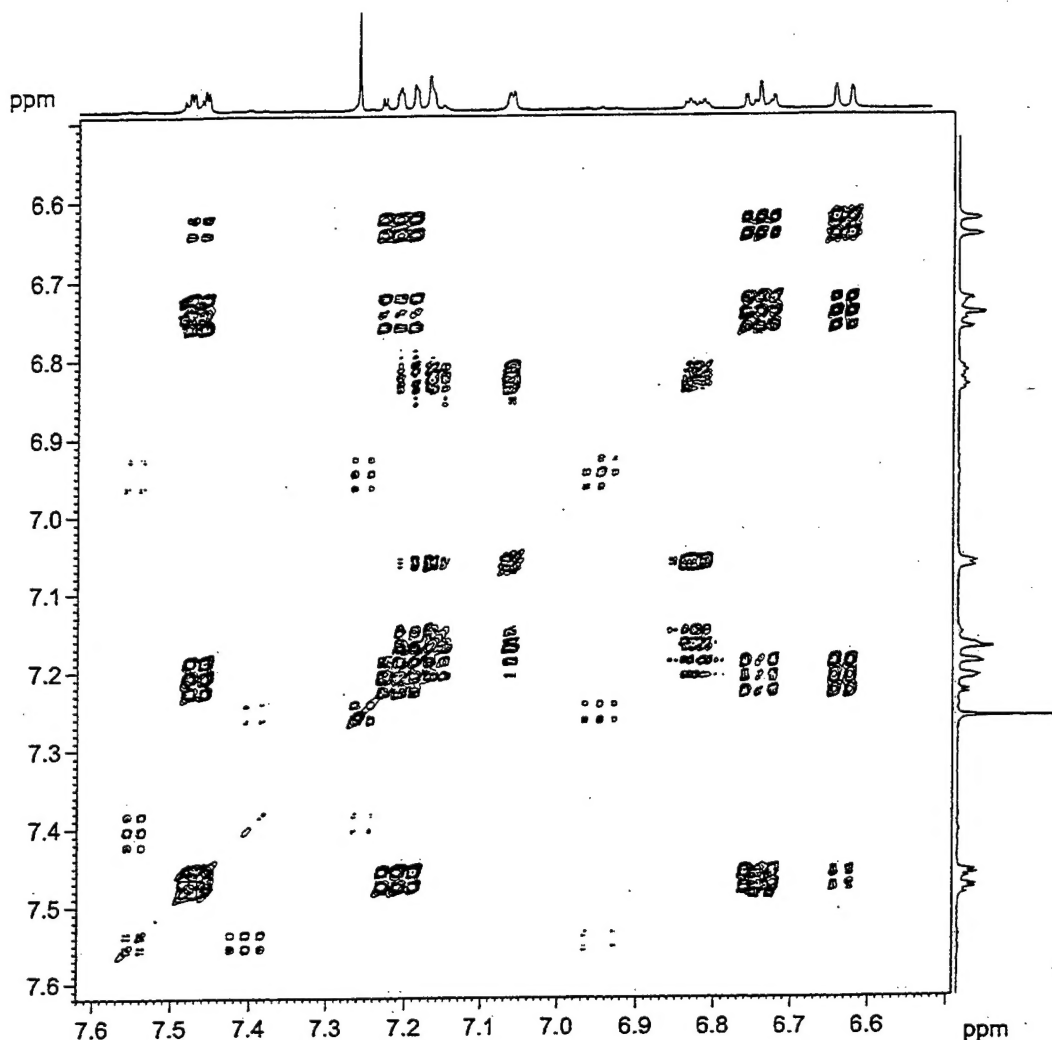


Figure 4 Proton NMR of POSS aniline monomer 4(top) and COSY spectrum (bottom)

The isolation of the free base form was confirmed via a sequential addition of HCl to the POSS aniline 4. The NH_2 registers as a relatively sharp peak at 4 ppm.(Figure 5) Upon addition of 0.1 equivalent aliquots of acid, the NH_2 peak is seen to broaden due to proton exchange among the protonated and free amines. The peak shifts downfield upon addition of acid due to the partial positive charge on the protonated amine. However, the peak with progressively narrows as the acid content is increased due to the lessened probability of exchange. Finally, at one equivalent of acid the amine peak is seen to be relatively sharp at occurs at 10.8 ppm. It is anticipated that the NH_2 peak will not significantly change upon further addition of acid.

The phenyl proton portion of the spectrum also demonstrates changes upon sequential addition of acid.(Figure 5) The POSS cage is electron withdrawing, and would have resonance stabilization with ortho and para amines, thus decreasing the basicity. As a result, the meta substituted amines are more basic, and are seen to shift downfield upon addition of small amounts of acid. The ortho and para peaks are also seen to shift

downfield upon addition of large amounts of acid. The large scale shifts can cause an appearance of splitting patterns in the phenyl proton resonances, which highlights the difficulty in isomer peak assignment.

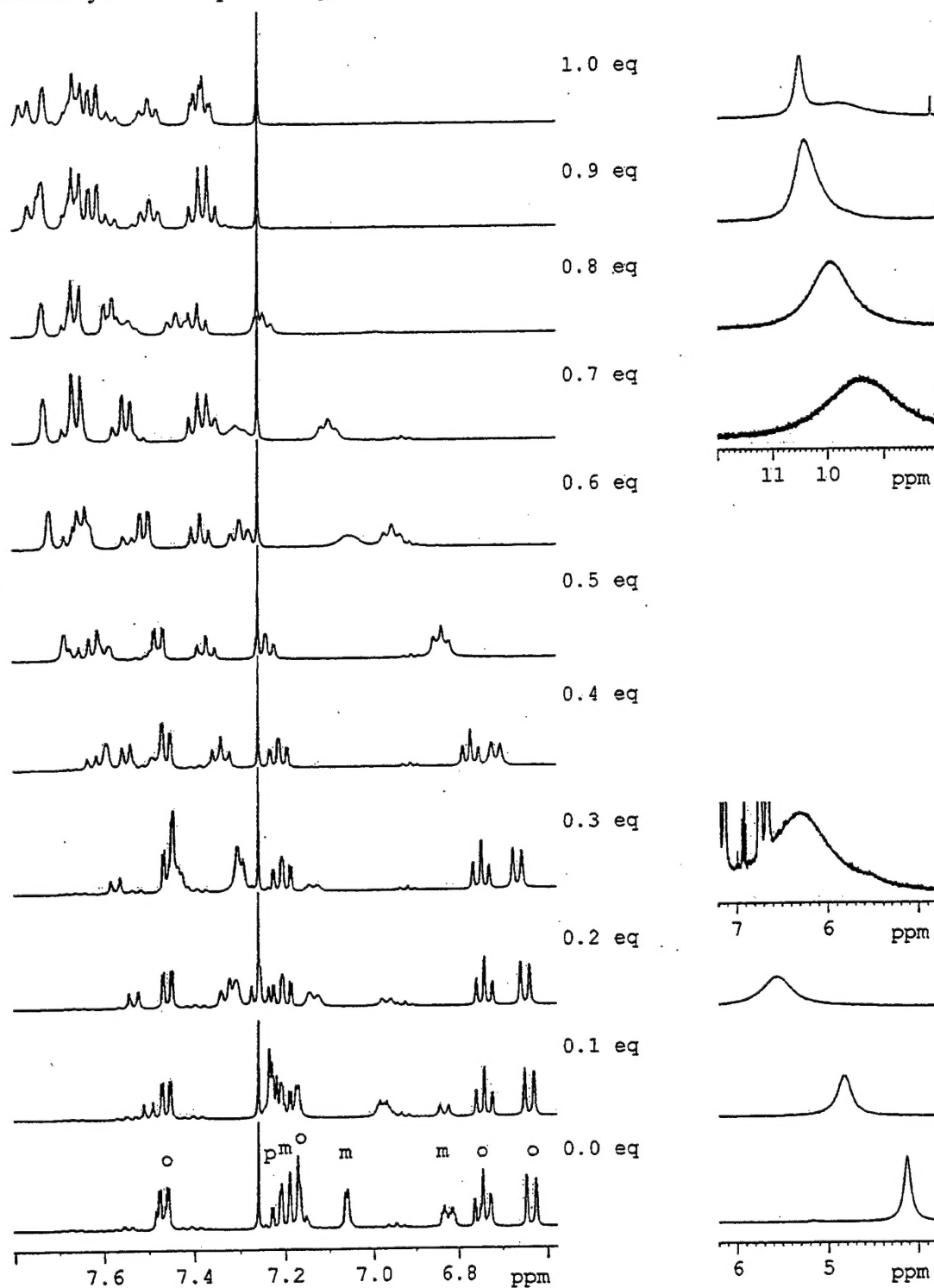


Figure 5 Sequential addition of acid to POSS aniline 4

Conclusions:

A model POSS aniline has been synthesized and characterized. Functionalizing the phenyl groups on a preformed POSS scaffold appears to be an efficient mechanism for forming mono -nitro and aminofunctional POSS. Mononitration and quantitative reduction to a monoamine was observed. Furthermore, the amine was isolated as the free base, and not as a salt. However, ^1H COSY NMR spectroscopy indicates that a variety of POSS aniline isomers are formed, ortho disubstitution most prevalent (57%), with meta (38%), and para (5%).

Acknowledgments:

We would like to thank Dr. Charles Lee (Air Force Office of Scientific Research) for support of this work. We also wish to thank Dr. Shawn Phillips and ~~Capt.~~ Steve Svejda for enlightening discussions. *Major*

References:

1. Lichtenhan, J.D., *Comments On Inorganic Chemistry*, 17(2): 115; (1995)
2. Wright, M; Feher, F.J.; Schorzman, D.A.; Jin, R.; submitted to *Macromolecules*; Phillips, S.H.; Gonzalez, R.I; Svejda, S.; Lichtenhan, J.; Provisional Patent Applied
3. Gonzalez, R. I. Ph.D.thesis, University of Florida, 2002
4. Tamaki, R., Tamaki, Y., Asuncion, M. Z., Choi, J; Laine, R. M. ; *J. Amer. Chem. Soc.*, **123**, 12416, (2001).
5. R.M. Laine, personal communication
6. Feher CF3 reference

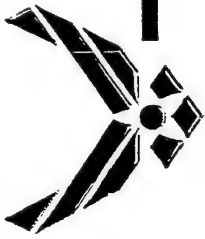
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Monofunctional Aminophenyl Polyhedral Oligomeric Silsesquioxanes (POSS) –A Model For High Performance Nanocomposite Monomers.

Brent D. Viers; Capt. Rene I. Gonzalez; Shawn H. Phillips;
Timothy Haddad

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Propulsion Materials Branch
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What is POSS

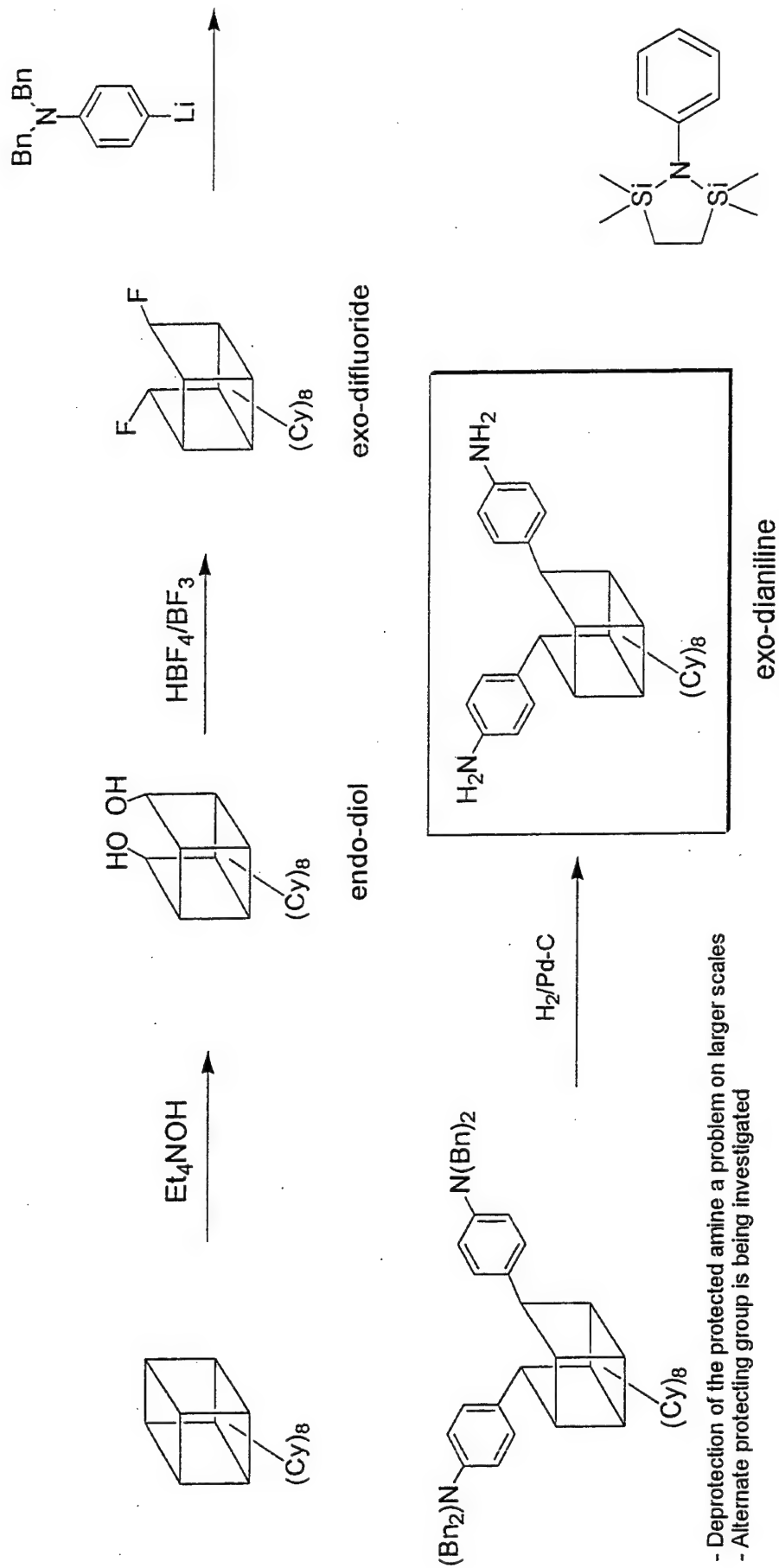


POSS=polyhedral oligomeric silsesquioxane

Insert POSS cartoons here



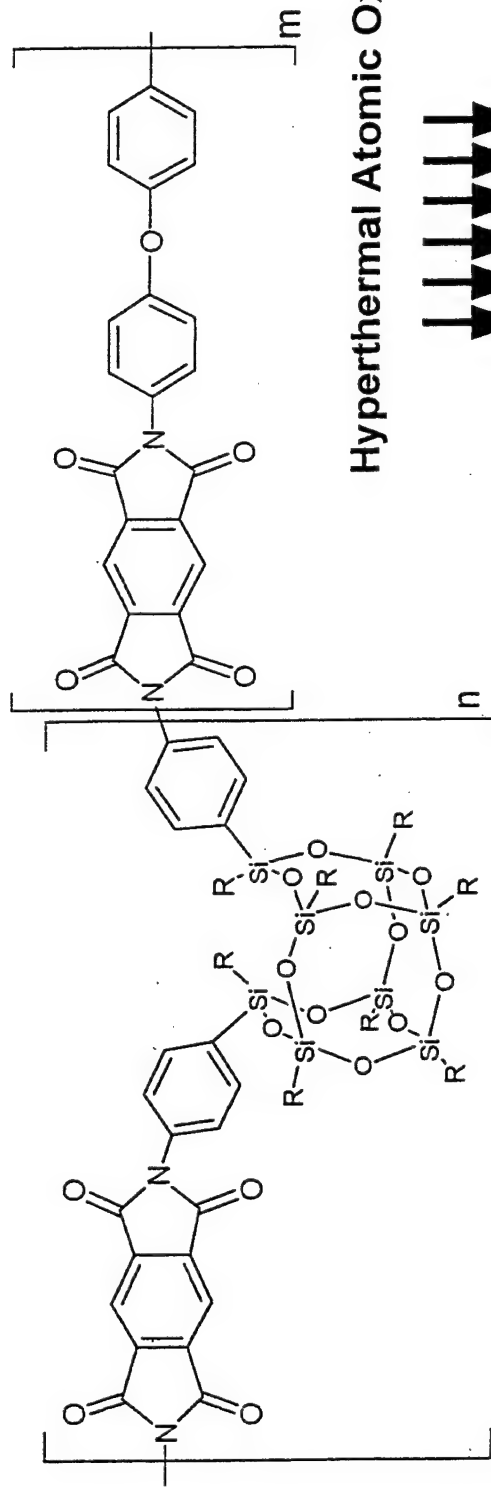
High Performance Dianiline



- Deprotection of the protected amine a problem on larger scales
- Alternate protecting group is being investigated



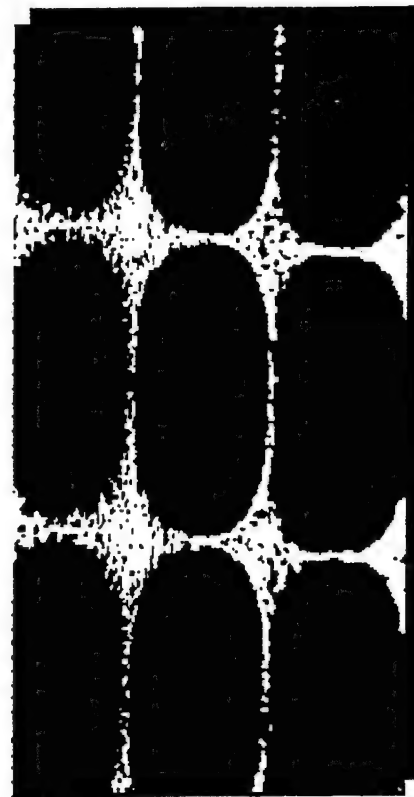
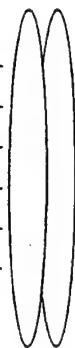
Space Resistant POSS-Kapton



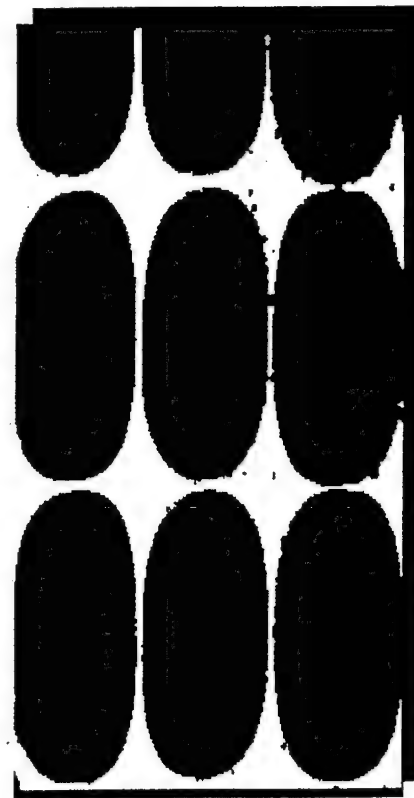
Hyperthermal Atomic Oxygen



Mask
Sample



Kapton H



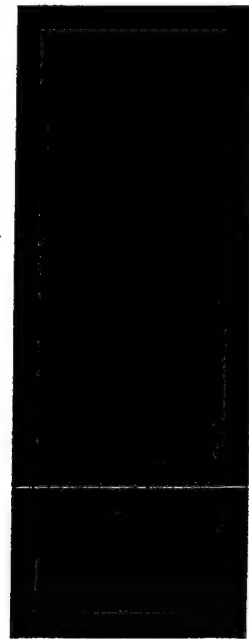
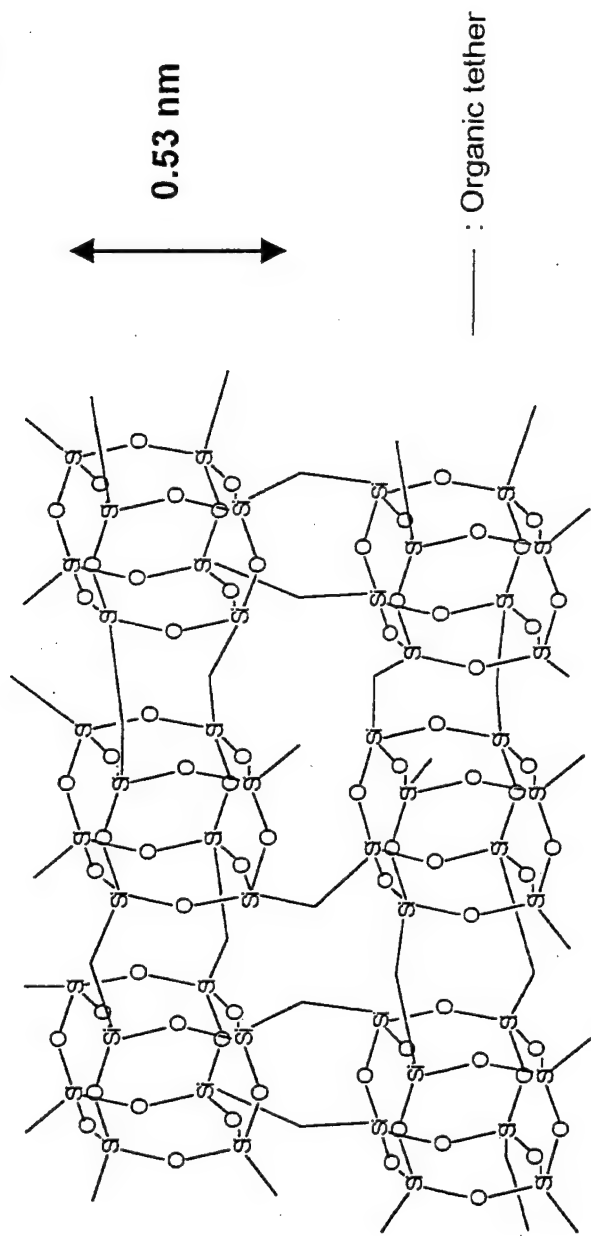
Kapton 10 wt% POSS



Tim Minton



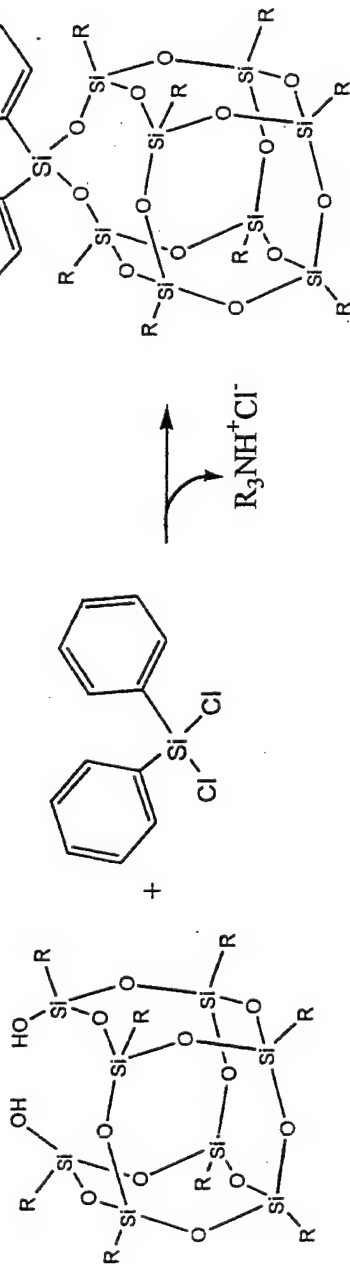
Laine's "Nanobricks"



Tamaki, R., Tamaki, Y., Asuncion, M. Z., Choi, J; Laine, R. M.
Octa(aminophenyl)silsesquioxane as a nanoconstruction site.
Journal of the American Chemical Society, **123**, 12416 - 12417, (2001).

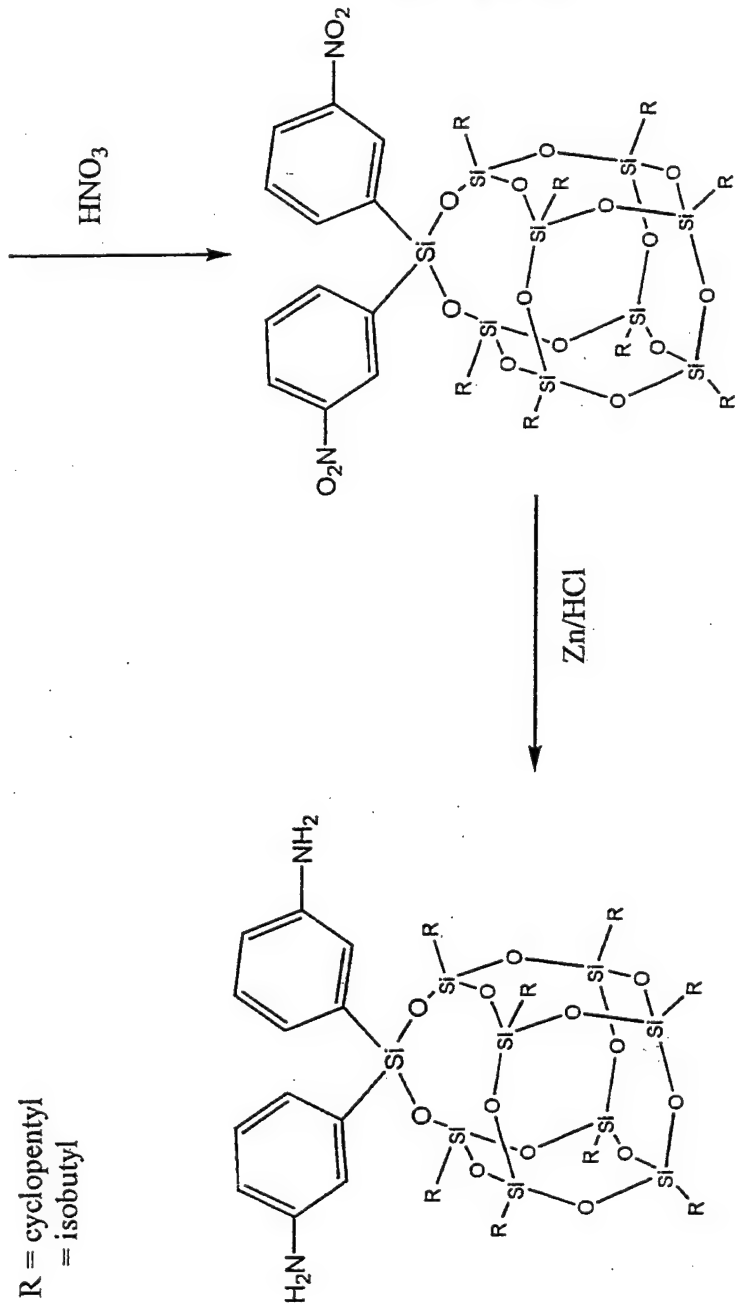


Improved Dianiline Scheme



Industrially
scalable

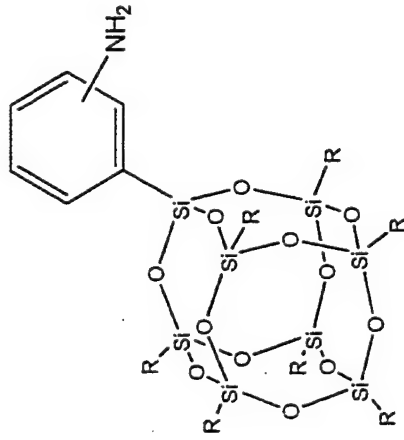
Less expensive
High performance
POSS comonomer



Meta substitution
assumed from aromatic
reactivity rules (EAS).



Model Amine compound

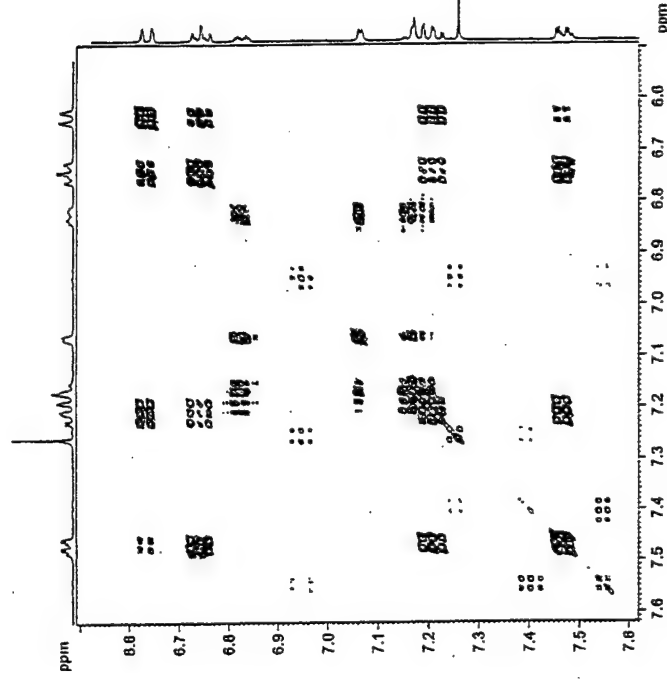
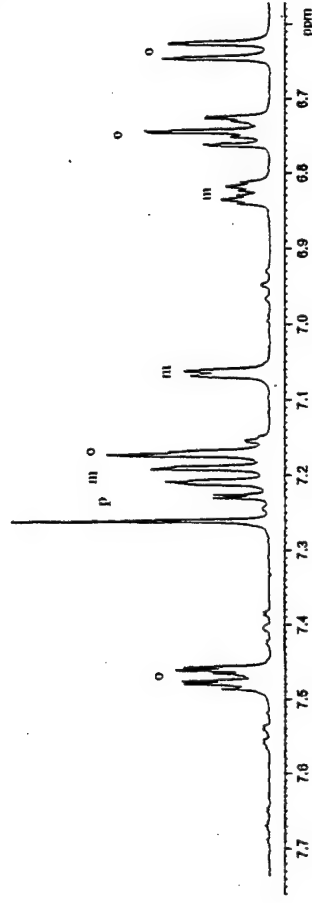


Cp₇T₈ aniline

57% ortho, 38 % meta, 5% para

Quantitative reduction of NO₂
Substitution ratios unchanged

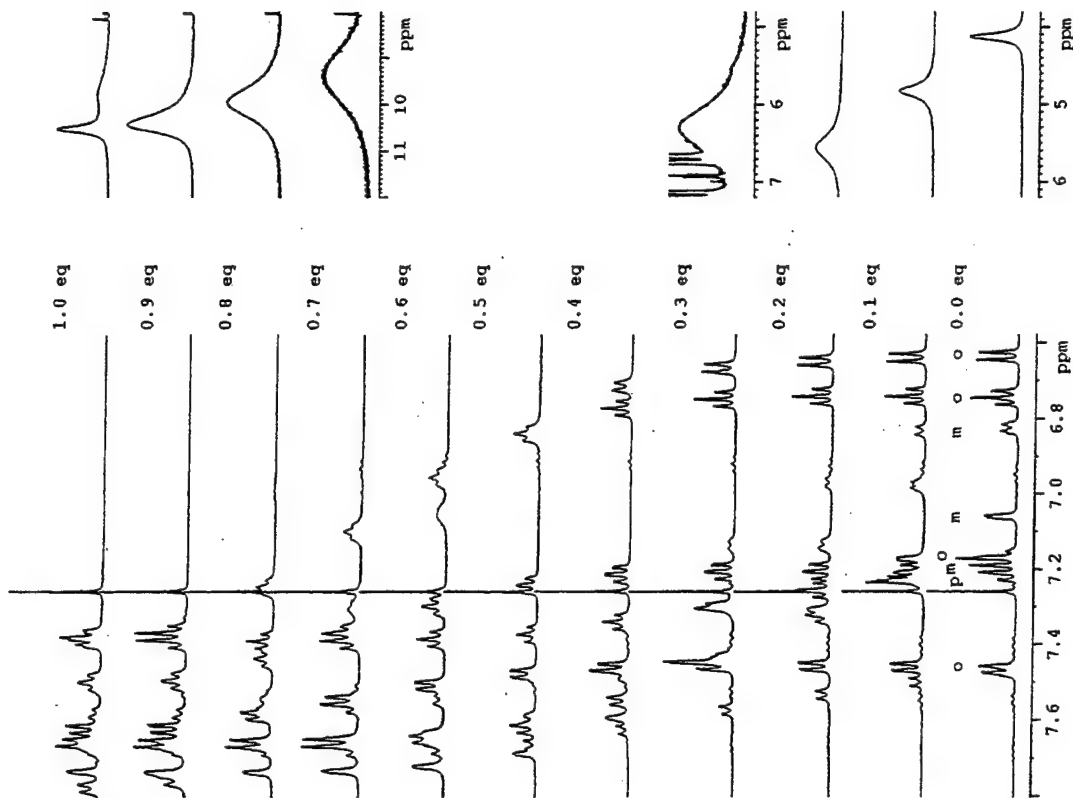
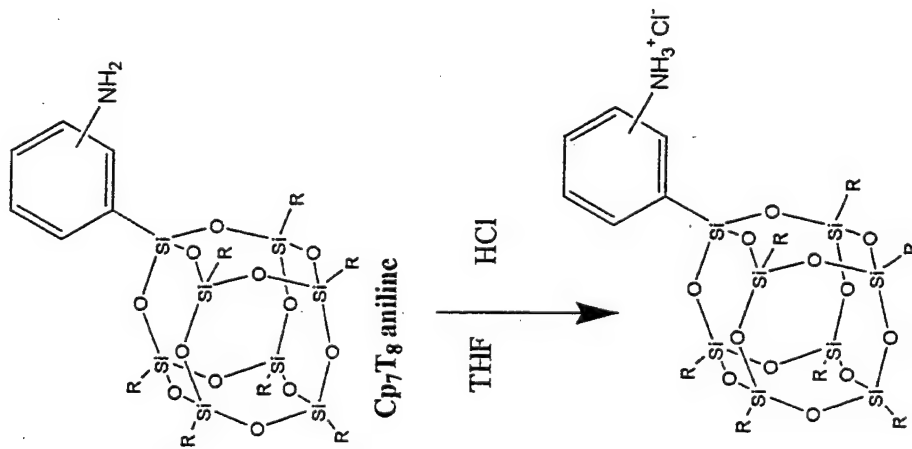
Model “bulky substituent”
reaction (phthalic anhydride)
underway

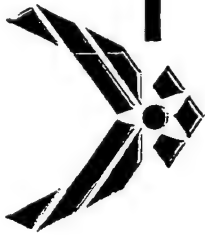


¹H COSY Spectrum

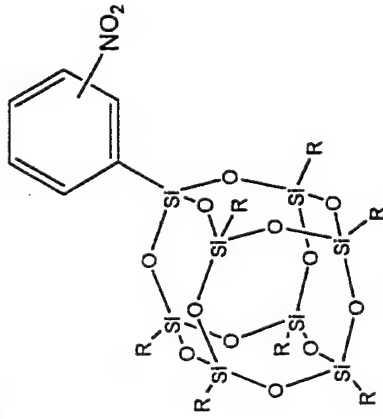


Isolation of the Free Amine





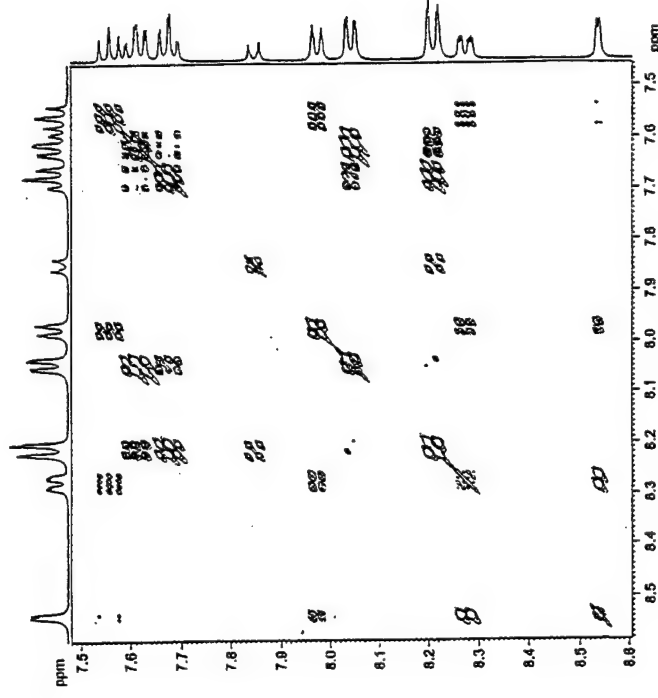
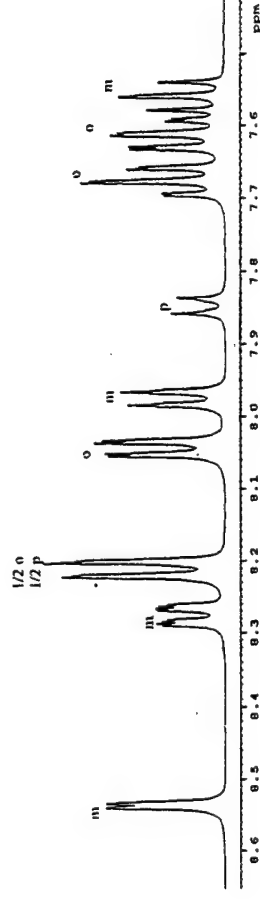
Model Nitro compound



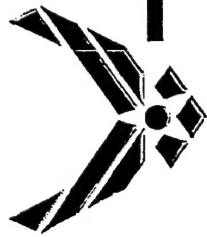
Cp₇T₈ Nitrobenzene

55% ortho, 37 % meta, 8% para

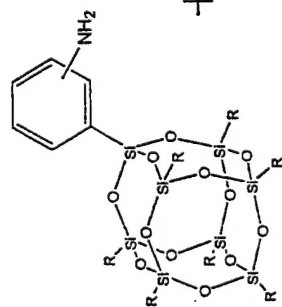
*Unexpected preponderance
of ortho species!*



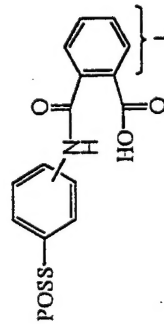
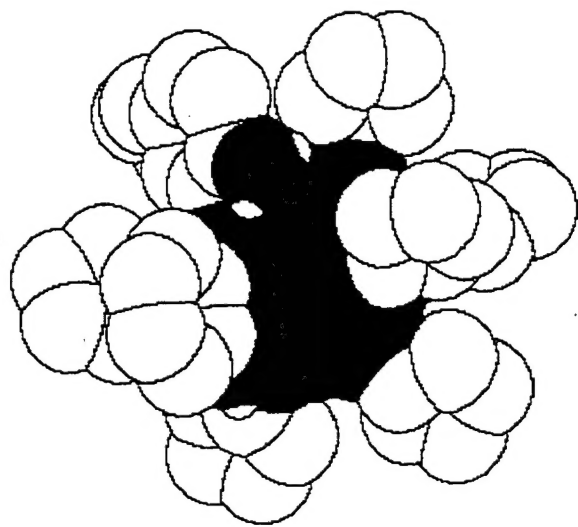
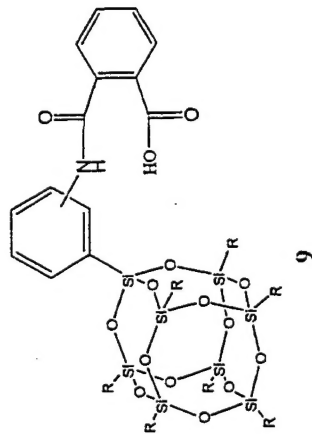
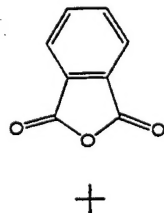
¹H COSY Spectrum



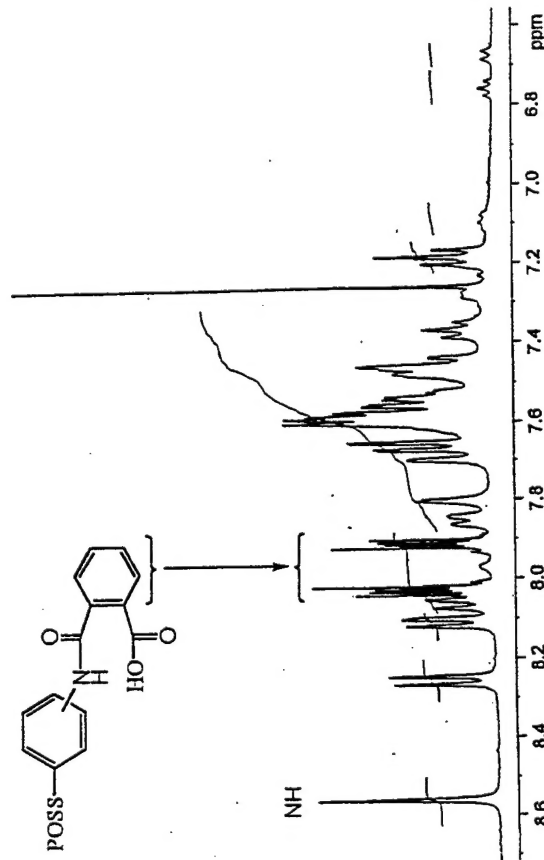
Sterically hindered Amines?



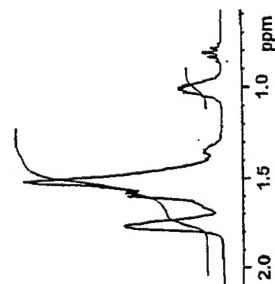
4: Cp7T8 aniline



NH



Si-(C₃H₉)



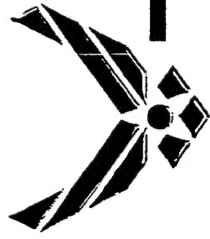


POSS based Polyimides



- Insert cartoon here





Conclusions



- Model aminophenyl POSS compounds synthesized
 - Mononitration
 - Quantitative reduction to free amine (aniline)
 - Unusual distribution of POSS-aniline isomers favors ortho substitution



Acknowledgments



- Charles Lee (AFOSR)
- Maj. Steve Svedja
- Professor Frank Feher
- Professor Gar Hoflund
- Professor Tim Minton

